

On the Lack of Conformational Preferences for Cyclic Dimethylsiloxane Oligomers

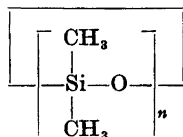
THOR ALVIK and JOHANNES DALE

Kjemisk Institutt, Universitetet i Oslo, Oslo 3, Norway

Cyclic dimethylsiloxane oligomers up to the hexadecamer have been isolated. Entropies and enthalpies of fusion, as well as infrared spectra, indicate that no conformational preferences exist in the liquid of the higher members. Only the trimer and the tetramer seem to have one well-defined conformation. The higher members (except the octamer) may have several conformations coexisting even in the crystal lattice. Trivial steric requirements of the methyl groups and the obtainment of high symmetry seem to dictate the selection of crystal conformation. Dielectric measurements do not permit calculation of dipole moments, as the high atomic polarization leads to molecular deformation in the electric field. Alternation in basicity along the series has been observed.

It is now well established that cycloalkanes and analogous heterocyclic compounds, containing for example amine nitrogen and ether oxygen, select, or strive towards, those ring conformations that can be derived from the diamond lattice.¹ This is a consequence of well-defined tetrahedral valency angles and relatively high torsional barriers in the ring bonds. The most notable examples of "saturated" rings which thus become conformationally homogeneous are those having six, ten, and fourteen ring atoms. Examples of rings that cannot find cyclic paths on the diamond lattice, and therefore become conformationally heterogeneous, are primarily those having an odd number of ring atoms. This leads in certain homologous series to interesting variations with ring size of physical properties that are sensitive to conformational homogeneity, such as the melting point.¹

A priori, one would hardly expect the ring skeleton of cyclodimethylsiloxanes



to show a similar tendency to follow a particular geometrical pattern. Dimethylsiloxanes are noted for their extreme molecular flexibility^{2,3} which impart to them outstanding properties, such as a low viscosity level,^{2,4} a small temperature coefficient for the viscosity,^{2,4} and high heat conductivity.³ The preferred valency angle at oxygen^{5,6} is unusually wide, about 140°, and can easily be further opened, so that in disiloxane itself⁷ even full inversion at oxygen is only hindered by a barrier of about 1.5 kcal/mol. No indication exists of a substantial torsional barrier in the Si–O bond.

Nevertheless, there remained a few observations that were tentatively explained by a similar tendency to assume a diamond-lattice geometry and the existence of preferred conformations.¹ Thus, the melting points of the cyclodimethylsiloxanes that had so far been isolated,^{8,9} as well as those of the closely related phosphonitrilic fluorides¹⁰ and chlorides,¹¹ show an alternation with ring size and a characteristic maximum for the octamer. This 16-membered ring is the first macrocyclic member of diamond-lattice geometry that would be free of intra-annular methyl interactions. Moreover, the crystal conformation of the octameric cyclodimethylsiloxane has in fact been found¹² to possess this geometry (Fig. 1). Of the other members, the tetramer has in the gas

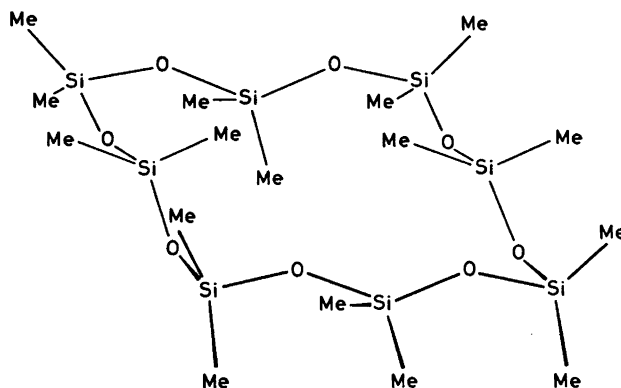


Fig. 1. The crystal conformation of hexadecamethylcyclooctasiloxane.¹²

phase¹³ the “saddle” conformation of D_{2d} symmetry (Fig. 2a) expected on the same basis, although in the low-temperature solid phase⁵ a “twist-chair” conformation of C_{2h} symmetry is found (Fig. 2b), which for a carbocyclic system would have a forbiddingly high energy.¹⁴

In order to elucidate more thoroughly this problem, it was necessary to extend the series to higher members and to base the discussion on measured enthalpies and entropies of melting instead of on their ratio, the melting temperature. Spectral properties, dipole moments and relative basicities might also yield information.

The six lowest members, from trimer to octamer, had been isolated earlier^{8,9} and certain of their physical properties measured.^{4,15} Later, it was demonstrated by analytical gas chromatography¹⁶ that equilibrium mixtures,^{17,18} obtained

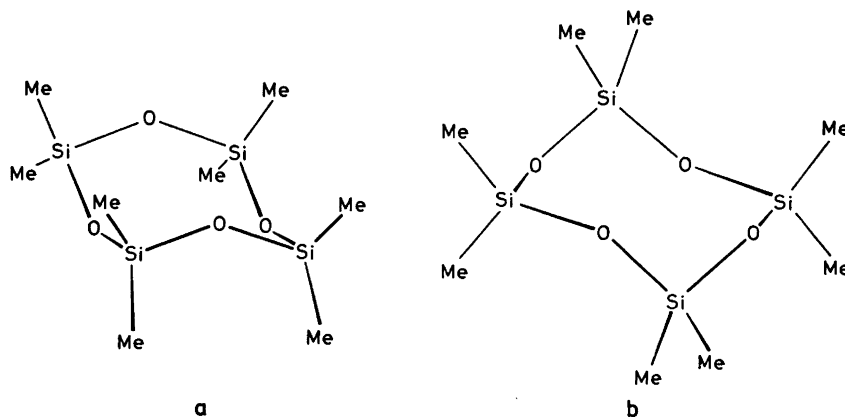


Fig. 2. The conformation of octamethylcyclotetrasiloxane as observed (a) in the gas phase¹³ and (b) in the low-temperature crystalline phase.⁵

by acid^{8,19} or base^{9,20} catalysis or by pyrolysis^{8,9} from dimethylsiloxane polymers, contain cyclic oligomers with up to 80 ring atoms (tetracontamer). Milligram quantities of rings with up to 50 ring atoms had earlier been collected¹⁷ for spectral characterization. We have now succeeded in isolating, by preparative gas chromatography of such equilibrium mixtures, larger quantities of all cyclic oligomers up to and including the hexadecamer (32-membered ring). The purity of all members up to the dodecamer (24-membered ring) was better than 99 %, and only these were investigated calorimetrically. The higher oligomers had a purity of about 98–99 % and did not crystallize even at -100° .

THERMAL PROPERTIES

The observed melting points are given in Fig. 3a, and the alternation noted earlier is seen to continue also for the higher members. A solid-solid transition point was observed only for three of the lower members; it was well separated from the melting point in the tetramer, and just below the melting point in the pentamer and hexamer.

The argument used earlier¹ to relate melting point alternation to an alternation of conformational homogeneity is based on the assumption that the enthalpy of melting increases regularly along a series, and that the alternation of melting temperature is produced by an alternation in the conformational part of the entropy of melting according to the relation

$$T_m = \Delta H_m / \Delta S_m$$

Thermal studies have so far been reported only for the trimer²¹ and the tetramer.^{21,22} The heats of melting (and transition) were now determined in a differential calorimeter, and the corresponding entropies of melting (and transition) were calculated. Only in the case of the tetramer could the heat

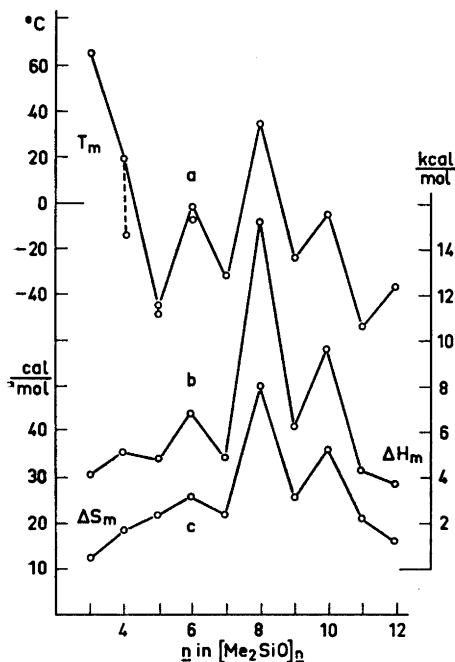


Fig. 3. Thermal properties of dimethylcyclosiloxane oligomers. (a) Melting and transition points. (b) The sum of enthalpies of melting and transition. (c) The sum of entropies of melting and transition.

of transition be determined without overlap with the heat of melting. As the heat of transition in all three cases is small (less than 30 % of the heat of melting), the sum of both are given in Fig. 3b. Similarly, the entropies of transition and melting are considered together and their sums given in Fig. 3c.

A strong alternation of the entropy of melting is indeed observed in the range from 10 to 22 ring atoms, but in the opposite sense of that expected. If the enthalpy of melting had been invariable, a large entropy change should have given a low melting point, and *vice versa*. But as the enthalpy of melting alternates even more strongly in the same sense, large entropies and enthalpies of melting go here together with high melting points.

An entropy of melting of the low order of magnitude expected for conformationally homogeneous rigid molecules, like the decalins²³ and 1,1,4,4,10,10,13,13-octamethylcyclooctadecane,²⁴ is observed only for the trimer, and this is in agreement with the lack of differences between the Raman spectra of solid, melt, and solutions.²⁵ The largest melting entropy, comparable even with that of the multiconformational open-chain hydrocarbon eicosane,²⁶ is observed for the octamer. The number of conformers in the liquid must therefore be very large, while on the other hand we know that the crystal contains only one conformer.¹² Strong conformational selection by the crystal lattice is also indicated by a marked simplification of the infrared spectrum on freezing (see the following paper, p. 2142). Since there is no *a priori* reason to expect that the number of liquid state conformers should be lower, and at least not very much lower, for the hepta- and nonamer, and not at all that

their number should decrease generally with increasing ring size, we are forced to conclude that all other higher oligomers have a mixture of conformers in their crystal lattice.

That the higher entropies of melting always go along with the higher enthalpies may be understood on the basis that when a ring of a given size out of several conformations has one that packs efficiently, the better van der Waals contacts and dipole interactions lead to a particularly low enthalpy in the crystal. This, in turn, then leads both to a high degree of conformational selection and to particularly small vibrational amplitudes of these otherwise flexible molecules. Both factors mean, of course, a strong entropy decrease on crystallization.

Since clearly one has in the cyclosiloxane field to abandon definitively the conformational principles used with much success in many carbocyclic series, another explanation for the alternation of thermal properties has to be sought. It seems natural to look at the possibility of forming highly symmetrical compact conformations, with efficiency of packing as the only criterion, and using as few types of monomer units as possible in order to obtain high symmetry. Considering each gem-dimethylsilicon group separately, the methyl groups can either be equivalent or non-equivalent. Using only units having equivalent methyl groups, ring structures must in general be planar, but valency angles then become too narrow at oxygen for the trimer and too wide at silicon already for the tetramer. The former must remain planar¹² and is therefore strained, while the latter can adjust the angles by puckering into a "saddle"¹³ with the oxygen atoms out of the plane of the silicon atoms (Fig. 2a).

A slight twist in direction towards a "boat" gives the S_4 -symmetry observed for cyclotetrasiloxane itself in the vapour,²⁷ for one of the conformers of the related and isostructural octamethylcyclotetrasilazane,²⁸ for octamethylcyclotetraphosphonitrile,²⁹ for the tetrameric phosphonitrilic dimethylamide,³⁰ and for the metastable form of tetrameric phosphonitrilic chloride.³¹

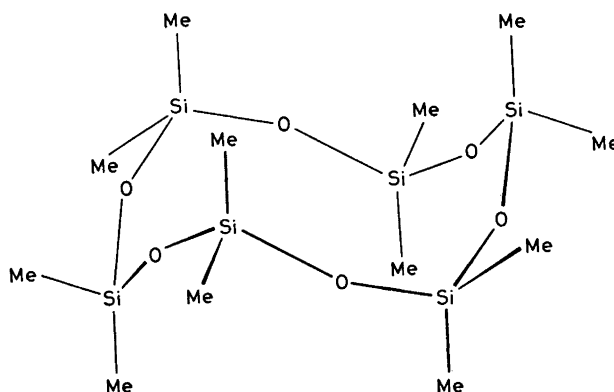


Fig. 4. Proposed crystal conformation for dodecamethylcyclohexasiloxane at low temperature (cf. Ref. 33).

In the pentamer such puckering cannot be symmetric, and the crystal structure of the related pentameric phosphonitrilic chloride³² illustrates the difficulties; it shows a very irregular roughly planar molecule, with valency angles at nitrogen varying from the normal 134° up to 159°.

Using only units having non-equivalent methyl groups, crown-like puckering becomes possible for rings with even n ; all oxygen atoms forming a plane and the silicon atoms lying alternately above and below, each having axial and equatorial methyl groups (Fig. 4). This is the crystal conformations to be expected for the siloxane hexamer at a sufficiently low temperature, in particular since this ring type is found in the crystal of the related hexameric phosphonitrilic dimethylamide.³³ Possibly the decamer has a similar conformation.

Finally, an alternation of both units leads to a high symmetry only when those units that have non-equivalent methyl groups also alternate between themselves in their relative orientation. This fits well for the tetramer, and the derived conformation is just the one observed for the low-temperature crystal phase of octamethylcyclotetrasiloxane⁵ (Fig. 2b), for the second of the two conformers of octamethylcyclotetrasilazane,²⁸ and for the stable form of tetrameric phosphonitrilic chloride.³⁴ This type also fits well for the octamer and is observed for the crystalline hexadecamethylcyclooctasiloxane¹² (Fig. 1). Extension to the dodecamer would give a too open structure.

Since the members with odd n , beyond the trimer, can have no puckered compact conformations of comparably high symmetry, the variations of thermal properties shown in Fig. 3 are qualitatively explained.

DIELECTRIC PROPERTIES

The dipole moments of molecules containing several polar groups very often yield useful information about molecular conformations. It was of interest in the present case to examine whether the dipole moment would increase regularly along the homologous series according to the relation

$$\mu_{\text{mol.}} = \sqrt{n} \mu_{\text{mon.}}$$

This would be expected³⁵ if the number of conformers in solution were so high, or the molecules so flexible, that on an average the orientation in the molecule of each "monomeric" dipole, with the value $\mu_{\text{mon.}}$, were independent of the others. If, however, the solution contained a predominance of the rigid crystal conformer, an alternation would be expected, since the members with even n should have either a center of symmetry, or D_{2d} symmetry, and therefore have internal compensation of the polar groups, while the members with odd n should in general have a resulting molecular moment.

Dipole moments have earlier been determined¹⁵ on the liquids for the lowest cyclodimethylsiloxanes ($n = 4 - 8$). Dielectric constants and refractive indices were now determined in benzene solution, and molecular dipole moments calculated according to the procedure of Hedestrand,³⁶ neglecting atomic polarization.

The results for the lower members are very close to those reported for the liquid state,¹⁵ and are shown in Fig. 5a together with the results for the higher members; they show a general increase with ring size. This increase follows the above quadratic relation with $\mu_{\text{mon.}} = 0.7$ D only above $n \sim 8$, while linear oligomers obey the same relationship for all members.¹⁵ The lower moments for the smaller rings must be due to a partial cancellation of dipoles, actually expected to be much more pronounced for rigid molecules. Nevertheless, a slight alternation is indeed observed and in the expected sense. However, when the method of calculating the dipole moments is looked at more critically, it will be seen (Fig. 5b and c) that the alternation is not present in the variable term (α_e) representing the total polarization, but is introduced by the variable term (α_n) representing the electronic polarization in the expression

$$\mu^2 = \frac{27kT}{4\pi N} \frac{1}{d_1(\epsilon_1 + 2)^2} (\alpha_e - \alpha_n)M_2$$

This is the reverse of a normal situation. The polarization due to dipole orientation is included in the total polarization, and, if alternating, should show up there, while the electronic polarization ought to increase regularly with ring size, as indeed observed for example in macrocyclic diesters and dilactones.³⁷ What is much worse, since the electronic polarization is known for the trimer³⁸ and tetramer^{22,38} to make up as much as 85 and 76 % of the total polarization, and we are not able to correct properly for the unknown atomic polarization, the error in the dipole moment may be enormous. A common procedure, which is to add 5–15 % to the electronic polarization, is here more than doubtful, as the atomic polarization of the trimer and tetramer has been shown³⁸ by microwave absorption to be particularly high, as much as 15 and 22 % of the total polarization, leaving only a few per cent, the difference between very large numbers, for the dipole orientation. This high contribution of the atomic polarization to the calculated apparent dipole moments in Fig. 5a indicates an unusual flexibility of siloxanes, as do many other properties already mentioned. Thus, the easy inversion of the Si–O–Si system⁷ can produce the equivalent of an orientation of the net dipole moment. To cite Dasgupta, Garg and Smyth,³⁸ “we enter a doubtful territory in which it may be difficult or arbitrary to distinguish between dipole orientation and atomic polarization”.

At most, it can be concluded qualitatively that the generally increasing moment along the series of cyclodimethylsiloxanes, and particularly the constancy of the total polarization term α_e (Fig. 5b) for rings higher than the octamer, suggests that each monomer unit behaves much as if it were independent and orients itself freely in the electric field. The resulting molecular conformation may then become very ill-defined, and a comparison with the static crystal conformation, or the conformation resulting in solution from the influence of polar solvent molecules, may be meaningless.

Also linear dimethylsiloxane oligomers³⁹ present a variation of the electronic polarization with molecular weight, but this is compensated by an opposite variation of an unusually large atomic polarization term (determined

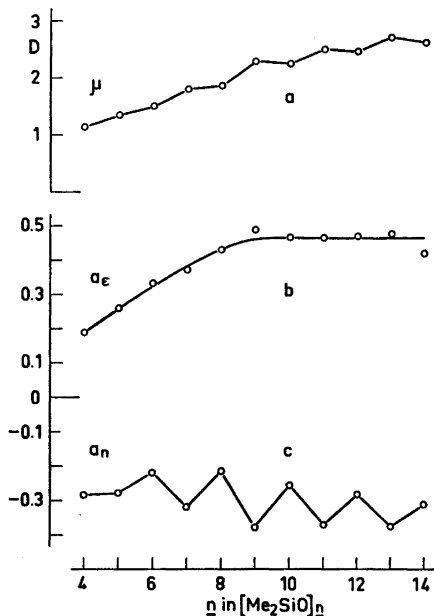


Fig. 5. Dielectric properties of dimethylcyclosiloxane oligomers. (a) Apparent molecular dipole moments in benzene solution. (b) Total polarization term a_ϵ = the slope of the straight line $f(w_2) = \epsilon_{1,2} - \epsilon_1$. (c) Electronic polarization term a_n = the slope of the straight line $f(w_2) = n_{1,2}^2 - n_1^2$.

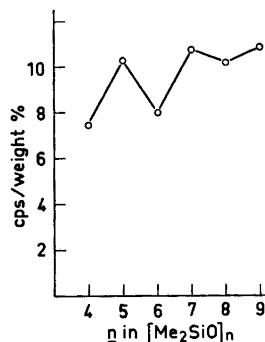


Fig. 6. Basicity of dimethylcyclosiloxane oligomers expressed as the slope of the curve relating the NMR chemical shift of phenolic OH with the weight percent of phenol in the siloxane.

from infrared dispersion) and the dipole polarization term, so that the total polarization per gram of material remains constant and independent of chain length.

RELATIVE BASICITIES

The presence of an alternation in molar refraction is in itself very interesting and may well be a manifestation of differences in the bonding situation at the oxygen atom. In the related cyclic phosphonitrile oligomers, the angle at nitrogen is markedly wider in the dichloro pentamer³² (up to 159°) than in the dichloro, the bis(dimethylamino), and the dimethyl tetramer²⁹⁻³¹ (up to 131°) and the bis(dimethylamino) hexamer³³ (148°). This goes together with an alternation in basicity along the phosphonitrilic chloride series,⁴⁰ those having odd n being least basic, except the trimer, which is more basic than all others. It seems natural to relate a large valency angle with delocalized electrons, hence low basicity and short bonds (*cf.* the pentameric phosphonitrilic chloride³²).

The basicity of the oxygen atom of siloxanes is known⁴¹ to be remarkably low. This has been explained⁴¹ on the one hand by the unavailability of the lone pair electrons, engaged in dative bonding with silicon, and manifested by the large Si—O—Si angle, and on the other hand by steric hindrance of the methyl groups. Since the importance of both factors should become reduced in small rings, the already known relatively higher basicity⁴¹ of the cyclodimethylsiloxane trimer is readily explained, the Si—O—Si angle being only 136°⁴² and the oxygen atoms quite exposed. It was therefore thought that any variation in conformation or bonding along the cyclic siloxane series might show up as a variation in oxygen basicity, similar to the alternation of nitrogen basicity found⁴⁰ in the cyclic phosphonitrilic chloride series.

Earlier comparisons of the basicity of the lower cyclic dimethylsiloxanes⁴¹ were based on infrared spectroscopic measurements of the strength of the hydrogen bonding between siloxanes and proton donors, such as phenol, but no significant variation with ring size was observed, except that the trimer was more basic than the next three members. A more sensitive method might be to look at the NMR chemical shift (at constant temperature) of the OH-proton when phenol was added to the liquid siloxane. Such a method had been used successfully⁴³ to determine relative basicities of aliphatic bases. Since the siloxanes are much less basic, it was necessary to use much greater excess of siloxane to prevent self-association of phenol. Extrapolation to infinite dilution met, however, with the difficulty that the NMR measurements became less reliable at the lowest concentrations, and the extrapolated values for all members were too close to tell anything about their relative magnitudes. More clear differences from one member to the next were noted in the displacement of chemical shift with concentration, which was linear below 4 % of phenol in siloxane. Comparative measurements in this concentration range gave a very steep curve for phenol in a weak base (heptane), whereas the curve was horizontal for phenol in a stronger base (tetrahydrofuran). The slope is thus a very sensitive measure of the ability of the base to compete with phenol itself as hydrogen acceptor. The values in Fig. 6 show that the tetra-, hexa-, and possibly the octamer are more basic than the penta-, hepta-, and nonamer. This is in agreement with a higher electron density on oxygen when the Si—O—Si angle is small, as it would be when ring puckering is most pronounced (even n). There is also agreement with steric effect considerations, as the oxygen atoms are more exposed in puckered rings. Roughly planar ring conformations for rings with odd n larger than the trimer (*cf.* pentameric phosphonitrilic chloride³²) would direct the apex of some of the oxygen atoms towards the ring center.

EXPERIMENTAL

Preparation and separation of cyclodimethylsiloxanes. The equilibrium mixture of cyclic oligomers was most conveniently obtained from a dimethylsiloxane polymer, Siloprene B, either by leaving a 30 % solution of the polymer in pentane for 2 days in the presence of 1 % concentrated sulfuric acid, or more simply by pyrolysis in vacuum at 400°. The product obtained by the latter method is the only one that contains the trimer in good yield; surprisingly it is also rich in high-boiling products. From the crude product, the most volatile part, containing from trimer to octamer, was then distilled off and further

fractionated by distillation and preparative gas-chromatography on a 20' \times 1/8" siloxane elastomer column, SE-30, 30 % on Celite, 60–80 mesh, temperature programmed from 50 to 300°. The residue was dissolved in benzene, and methanol added until polymer started to precipitate. The viscous liquid polymer was separated off, solvents evaporated, and the liquid distilled in vacuum through a very short column. The distillate contained oligomers up to the hexadecamer and was fractionated by preparative gas chromatography as above. To avoid aerosol formation, which prevented condensation, the traps were irradiated by an infrared lamp.

The purity of isolated oligomers was checked by analytical gas chromatography.

Calorimetric measurements. These were performed in a differential calorimeter constructed by Dr. Jean F. M. Oth, Union Carbide European Research Associates, Brussels. Very precise measurements could be obtained down to -100°C on 20–200 mg samples, sealed under vacuum in glass tubes. Both cooling and heating curves were recorded. Oligomers higher than the dodecamer showed no latent heats down to -100° .

Observed melting and transition temperatures and corresponding heats are given below. Calculated total entropies of melting and transition are given only in Fig. 3c.

<i>n</i> of oligomer	3	4	5	6	7	8	9	10	11	12
M.p ($^{\circ}\text{C}$)	64.0	17.3	-47	-4.2	-35.5	31.5	-27	-7.4	-57	-39
Tr.p. ($^{\circ}\text{C}$)		-16.2	-48.5	-8.0						
ΔH_m (cal/mol)	4166	4055			4990	15136	6129	9502	4238	3692
ΔH_{tr} (cal/mol)		1144	4869	6830						

Determination of dipole moments. Dielectric constants were measured at 20° in a Weilheim Dipolmeter DM 01 on four different solutions of each compound. Concentrations were in the range of 20–200 mg of siloxane in about 30 g of benzene. Refractive indices at the sodium D line were measured on the same solutions in a Bausch & Lomb Refractometer. Calculation of apparent dipole moments were performed according to Hedestrand,⁸ using no correction for atomic polarization.

Determination of relative basicities by NMR-spectroscopy. The siloxane was weighed into an NMR-tube, and the phenol added in weighed portions before each measurement of chemical shift in a Varian A 60 A spectrometer. As a reference for the OH signal, the strongest and sharpest signal for the aromatic CH-protons of the phenol was used, and the distance noted in cps. The temperature was kept at $38 \pm 1^{\circ}$, and the shift variation with temperature was shown to be 0.9 cps per $^{\circ}\text{C}$. The observed shift difference for four or five solutions, containing from 0.2 to 5 % by weight of phenol in the siloxane, were plotted and extrapolated to zero concentration. The extrapolated values and curve slopes are given below:

<i>n</i> of oligomer	4	5	6	7	8	9	10	11	12
Extrapolated shift (cps)	98.3	94.3	93.7	92.0	90.0	89.0	168	168	168
Slope (cps/% by w. of phenol)	7.5	10.3	8.0	10.8	10.2	10.9	25.5	25.5	25.5
								tetra- hep- tane	hydro- furan
									-72
									~ 0

Acknowledgements. We thank Dr. Jean F. M. Oth, Brussels (now Zürich), for his help in letting us use his calorimeter, the *Alf Bjerckes Legat* for financial support (to Thor Alvik), and Dr. Thor Gramstad, Kjeller (now Bergen), for his help in the determination of dipole moments.

REFERENCES

1. Dale, J. *Angew. Chem.* **78** (1966) 1070.
2. Bondi, A. *Ann. N.Y. Acad. Sci.* **53** (1951) 870.
3. Bondi, A. *J. Chem. Phys.* **19** (1951) 128.
4. Hurd, C. B. *J. Am. Chem. Soc.* **68** (1946) 364.
5. Steinfink, H., Post, B. and Fankuchen, I. *Acta Cryst.* **8** (1955) 420.
6. Damaschun, G. *Kolloid Z.* **180** (1962) 65.

7. Aronson, J. R., Lord, R. C. and Robinson, D. W. *J. Chem. Phys.* **33** (1960) 1004.
8. Patnode, W. and Wilcock, D. F. *J. Am. Chem. Soc.* **68** (1946) 358.
9. Hunter, M. J., Hyde, J. F., Warrick, E. L. and Fletcher, H. J. *J. Am. Chem. Soc.* **68** (1946) 667.
10. Chapman, A. C., Paddock, N. L., Paine, D. H., Searle, H. T. and Smith, D. R. *J. Chem. Soc.* **1960** 3608.
11. Lund, L. G., Paddock, N. L., Proctor, J. E. and Searle, H. T. *J. Chem. Soc.* **1960** 2542.
12. Frevel, L. K. and Hunter, M. J. *J. Am. Chem. Soc.* **67** (1945) 2275.
13. Yokoi, M. *Bull. Chem. Soc. Japan* **30** (1957) 100.
14. Hendrickson, J. B. *J. Am. Chem. Soc.* **89** (1967) 7036.
15. Sauer, R. O. and Mead, D. J. *J. Am. Chem. Soc.* **68** (1946) 1794.
16. Carmichael, J. B., Gordon, D. J. and Ferguson, C. E. *J. Gas Chromatogr.* **4** (1966) 347.
17. Brown, J. F. and Slusarczyk, G. M. *J. Am. Chem. Soc.* **87** (1965) 931.
18. Carmichael, J. B., Gordon, D. J. and Isackson, F. J. *J. Phys. Chem.* **71** (1967) 2011.
19. Hurd, D. T. *J. Am. Chem. Soc.* **77** (1955) 2998.
20. Hurd, D. T., Osthoff, R. C. and Corrin, M. L. *J. Am. Chem. Soc.* **76** (1954) 249.
21. Osthoff, R. C., Grubb, W. T. and Burkhard, C. A. *J. Am. Chem. Soc.* **75** (1953) 2227.
22. Hoffmann, J. D. *J. Am. Chem. Soc.* **75** (1953) 6313.
23. McCullough, J. P., Finke, H. L., Messerly, J. F., Todd, S. S., Kincheloe, T. D. and Waddington, G. *J. Phys. Chem.* **61** (1957) 1105.
24. Borgen, G. and Dale, J. *Chem. Commun.* **1969** 447.
25. Kriegsmann, H. *Z. anorg. allgem. Chem.* **298** (1959) 223.
26. Schaerer, A. A., Busso, C. J., Smith, A. E. and Skinner, L. B. *J. Am. Chem. Soc.* **77** (1955) 2017.
27. Glidewell, C., Robiette, A. G. and Sheldrick, G. M. *Chem. Commun.* **1970** 932.
28. Smith, G. S. and Alexander, L. E. *Acta Cryst.* **16** (1963) 1015.
29. Dougill, M. W. *J. Chem. Soc.* **1961** 5471.
30. Bullen, G. J. *Proc. Chem. Soc.* **1960** 425.
31. Hazekamp, R., Mighelsen, T. and Vos, A. *Acta Cryst.* **15** (1962) 539.
32. Schlueter, A. W. and Jacobson, R. A. *J. Am. Chem. Soc.* **88** (1966) 2051.
33. Wagner, A. J. and Vos, A. *Acta Cryst.* **B 24** (1968) 1423.
34. Wagner, A. J. and Vos, A. *Acta Cryst.* **B 24** (1968) 707.
35. Smyth, C. P. *Dielectric Behavior and Structure*, McGraw, New York 1955, p. 371.
36. Hedestrand, G. *Z. Physik. Chem.* **B 2** (1929) 428.
37. Dale, J. *J. Chem. Soc.* **1965** 72.
38. Dasgupta, S., Garg, S. K. and Smyth, C. P. *J. Am. Chem. Soc.* **89** (1967) 2243.
39. Baker, E. B., Barry, A. J. and Hunter, M. J. *Ind. Eng. Chem.* **38** (1946) 1117.
40. Brion, C. E., Oldfield, D. J. and Paddock, N. L. *Chem. Commun.* **1966** 226.
41. West, R., Whatley, L. S. and Lake, K. J. *J. Am. Chem. Soc.* **83** (1961) 761.
42. Peyronel, G. *Atti Accad. Nazl. Lincei, Rend., Cl. Sci. Fis. Mat.* **16** (1954) 78, 231.
43. Socrates, G. *Trans. Faraday Soc.* **63** (1967) 1083.

Received November 30, 1970.